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DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371U.S. APPLICATION NO. (If known, see 37
CFR 1.5) (Not Yet Assigned - U.S. National
Phase of Int'l PCT)

10/031472

INTERNATIONAL APPLICATION
NO. PCT/FR00/02197INTERNATIONAL FILING DATE
July 31, 2000PRIORITY DATE CLAIMED
August 3, 1999TITLE OF INVENTION: STOPPER INCORPORATING A COMPOSITION OR PREBLEND BASED ON
VOLATILE CORROSION INHIBITORS

APPLICANT(S) FOR DO/EO/US Gabriela STOIANOVICI, Loïc GUILLOU and Patrick DRONIOU

Applicant herewith submits to the United States Designated/Elected Office(DO/EO/US) the following items and other information:

1. This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l).
4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. has been transmitted by the International Bureau.
 - c. is not required, as the application was filed in the United States Receiving Office (RO/US).
6. A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. have been transmitted by the International Bureau.
 - c. have not been made; however, the time limit for making such amendments has NOT expired.
 - d. have not been made and will not be made
8. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). (Executed)
10. A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. An Information Disclosure Statement under 37 CFR 1.56, 1.97 and 1.98 with PTO Form 1449 attached;
12. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. A **FIRST** preliminary amendment.
 - A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. A substitute specification.
15. A change of power of attorney and/or address letter.

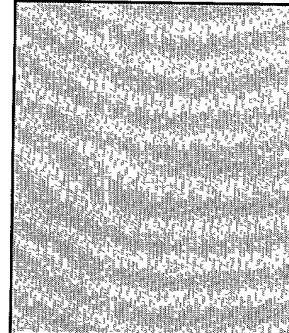
16. Other items or information:

PCT International Application Published Under the Patent Cooperation Treaty (Cover Page);
PCT International Search Report (Form PCT/ISA/210);
PCT Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).
PCT Request (Form PCT/RO/101)

17. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):

Search report has been prepared by the EPO or JPO \$ 890.00
 International preliminary examination fee paid to USPTO (37 CFR 1.482) \$
 No international preliminary examination fee paid to USPTO (37 CFR 1.482
 but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$
 Neither international preliminary examination fee (37 CFR 1.482) nor
 international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$
 International preliminary examination fee paid to USPTO (37 CFR 1.482)
 and all claims satisfied provision of PCT Article 33(2)-(4) \$



ENTER APPROPRIATE BASIC FEE AMOUNT =

\$890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than
 20 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

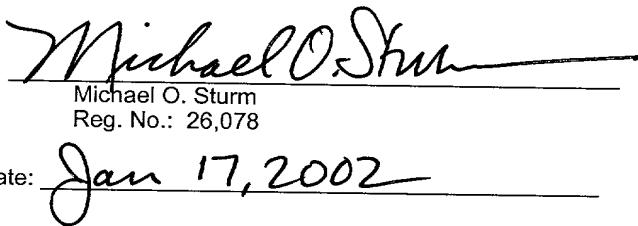
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CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total Claims	11 -20 =	0	X \$18.00	\$0.00
Independent Claims	1 - 3 =	0	X \$84.00	\$ 0.00
Multiple dependent claims(s) (if applicable)	Yes		+ \$280.00	\$280.00
TOTAL OF ABOVE CALCULATIONS =				\$1,170.00
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$0.00
SUBTOTAL =				\$1,170.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$0.00
TOTAL NATIONAL FEE =				\$1,170.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31).				
\$ 40.00 per property +				\$ 40.00
TOTAL FEES ENCLOSED =				\$1,210.00
				Amount to be:
				refunded \$
				charged \$

- A check in the amount of \$ 1,210.00 to cover the above fees is enclosed.
- Please charge my Deposit Account No. 08-1650 in the amount of \$ to cover the above fees. A duplicate copy of this sheet is enclosed.
- The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 08-1650.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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CERTIFICATION OF TRANSLATION

I, BANHOLZER Vivien, of CABINET PLASSERAUD, 84, rue d'Amsterdam, 75440 PARIS CEDEX 09, FRANCE, do hereby declare that I am well acquainted with the French and English languages, and verify that the document attached is a true English language translation of the text of International Patent Application no. PCT/FR00/02197.

Dated this 04th January 2002



BANHOLZER Vivien

**STOPPER INCORPORATING A COMPOSITION OR PREBLEND BASED
ON VOLATILE CORROSION INHIBITORS**

The invention relates to polymer-based
5 stoppers, one of the components of which consists of a composition or preblend based on volatile corrosion inhibitors.

The invention also relates to the use of the abovementioned stoppers for the internal protection of
10 hollow metal components against corrosion.

In the present invention, the term "stopper" means any component capable of obstructing the opening of a hollow component, such as stoppers, capsules, threaded bodies, used for the localized volatile anti-corrosion protection of certain hollow internal parts
15 of metal components.

The material constituting the polymer-based stoppers, one of the components of which consists of a composition or preblend based on volatile corrosion inhibitors, has been used to prepare wrapping articles.
20

Specifically, it is known practice to use volatile corrosion inhibitors when it is a matter of protecting against the corrosion of corrosion-sensitive metal components, in particular those made of mild
25 steel with a low carbon content and which, once machined, are dispatched in their given form to their place of destination in a shipping container for the purpose of finishing on site, in particular by painting; the risks of corrosion are thus considerable,
30 especially when the components in question are sent to hot and humid regions.

For example, when the metal components to be protected are wrapped in films, VCIs are incorporated into the material constituting these films; given that
35 these films can come into direct contact with the surface of the components to be protected, corrosion inhibitors which act by contact are also incorporated into the mass constituting these films.

Under these conditions, volatile corrosion
40 inhibitors offer very good protection against corrosion

and have the advantage of making it possible to avoid the use of conventional techniques for protecting metal components; these conventional techniques consist in applying paints, varnishes, plastics, waxes, greases 5 and oils, which should be removed before the on-site finishing, thus entailing additional costs and pollution.

Volatile corrosion inhibitors, generally referred to as VCIs, incorporate additives whose vapour 10 pressure can be considered as non-negligible at the working temperature (for example from about 10^{-5} to 10^{-1} mmHg, at 20°C), and which are capable of inhibiting the corrosion of metals.

These VCIs act by virtue of the fact that they 15 are conveyed in vapour form to the metal surface to be protected, in order to be adsorbed thereon or dissolved in condensation water, if any.

Products are also known which are classified by extension in VCIs on account of the fact that one of 20 their reaction products has an adequate vapour pressure. Thus, for example, sodium nitrite, in the presence of ammonium ions, can form ammonium nitrite which is relatively volatile. The starting sodium nitrite is thus considered as a VCI.

It is occasionally necessary to corrosion-protect only the internal parts of large-sized hollow metal components of complex geometry, in particular cavities, threaded parts or tubular holes. Stoppers in accordance with this invention, based on polymers and 30 optionally on other structuring agents, shaped by the usual techniques of the polymer industry (extrusion, injection-moulding, thermoforming) make it possible to obstruct the openings of the metal components and provide them with the required localized protection, 35 thus considerably minimizing the costs.

In order to incorporate VCIs into the material constituting wrappings, in particular films which are often based on thermoplastic polymers, it is known practice to prepare direct mixtures of VCI powders with

the polymers and to form the articles in question directly by extrusion or injection-moulding.

At the extrusion temperature, which is about 160°C for low-density polyethylene and 240°C for 5 polypropylene, VCIs are extremely volatile, and this leads, in the case of articles of low thickness, to the appearance of high porosity and to a strong risk of degradation and/or decomposition with removal of at least some of the VCIs. The efficacy from the point of 10 view of the anticorrosion of such articles is thus greatly reduced as a result of the loss of active material.

To overcome this drawback, i.e. to limit the loss of VCIs during the actual preparation of the 15 articles, it has been proposed to provide preblends containing VCIs, i.e. concentrates of active material dispersed in supports such as polymers, solvents and plasticizers; polymer-based preblends (patent BR-A-9001035) have the general advantage of being 20 homogeneous and easy to handle; these preblends are then incorporated into the polymers for the purpose of preparing articles.

Given, however, that the temperatures used at the time of preparation of the preblends are often 25 greater than 150°C, at least partial degradation of the said preblends occurs; thus, for example, it is noted that dicyclohexylamine nitrite, mixed and extruded with polyethylene at 160°C, gives preblend granules which have a dark yellow colour, characteristic of extensive 30 degradation, i.e. a loss of activity.

To avoid these excessive thermal degradations, it has been proposed to use liquid preblends, based on oil, which do not need to be taken to high temperatures during their manufacture (patent US-A-4 913 874).

35 However, given that VCIs are rarely soluble in these oily media, this results in heterogeneity of the preblends obtained and the occurrence of difficulties due to local superconcentrations or under-

concentrations during their subsequent incorporation into the polymers from which the articles are made.

It has also been proposed to overcome this drawback by using liquid preblends in the form of 5 solvent-based or oily solutions comprising the VCIs, these preblends not being incorporated during the extrusion, but applied to films by spraying, thus forming, after evaporation of the solvent, either a powdery layer of VCI (patent DE 3 417 149 A1) or an 10 oily layer containing the VCIs (patent GB 2 188 274 A).

The drawback of these preblends lies in the fact that the VCIs are not imprisoned in a matrix imposing slow release, and the protection obtained is thus short-lived. Moreover, the adhesion of the layers 15 deposited onto the articles is low and leads to losses during manipulation and to the need to clean the components that are to be protected, which is precisely what one would wish to avoid.

The aim of the invention is to provide stoppers 20 based on polymers using at least one VCI-based composition, which satisfy the various practical requirements better than those already existing.

An object of the invention is also to propose novel uses for these VCI-based stoppers, such as the 25 partial and localized protection of certain internal parts of hollow metal components.

Following extensive research, the Applicant Company has now, to its credit, found that these aims can be achieved if stoppers are used based on polymers 30 incorporating a composition based on volatile corrosion inhibitors which comprises structuring agents capable of allowing the preparation of a preblend at temperatures that are low enough to limit the release and/or degradation of these VCIs as much as possible 35 during this preparation.

Consequently, the polymer-based stoppers in accordance with the invention are characterized in that they incorporate a composition based on volatile corrosion inhibitors which comprises an effective

amount of at least one structuring agent, consisting of a solid or pasty substance whose melting point is from 40 to 110°C, preferably from 50 to 90°C, by means of which the release and/or degradation of the VCIs at the 5 time of formation of the composition or preblend is limited as much as possible.

According to one advantageous embodiment, the composition used in the stoppers in accordance with the invention comprises from 1 to 90%, preferably from 10 to 60%, by weight of at least one volatile corrosion inhibitor and from 10 to 99%, preferably from 40 to 80%, of at least one structuring agent consisting of a solid or pasty substance whose melting point is from 40 to 110°C, preferably from 50 to 90°C.

15 According to another advantageous embodiment, the composition used in the stoppers in accordance with the invention comprises at least one structuring agent chosen from the group comprising solid or pasty, aliphatic and/or resinous compounds with a low melting 20 point of between 40 and 110°C, preferably between 50 and 90°C.

According to another advantageous embodiment of the composition used in the stoppers according to the invention, the structuring agent is chosen from the 25 group comprising mono- or polyfunctional aliphatic organic compounds which are linear and/or slightly branched with hydrocarbon-based chains containing at least 10 carbon atoms, including, in particular:

30 - saturated or unsaturated, optionally oxidized mono- or dicarboxylic acids, their esters and their salts,

35 - phosphoric, sulphonic and phosphonic acids, their esters with alcohols and their alkali metal, alkaline-earth metal, zinc, aluminium and/or organic amine salts,

- cyclic or acyclic compounds of the group comprising lactones, ketones, aldehydes, amides and acetals,

- optionally polyalkoxylated, cyclic or acyclic, primary or secondary higher alcohols with a hydrocarbon-based chain containing at least 10 carbon atoms,

5 - linear and/or slightly branched aliphatic hydrocarbons, in particular paraffins and isoparaffins,
- polyolefins and their copolymers with low molecular masses from 3000 to 20,000 g/mol,
- polyglycols, in particular polyethylene
10 glycols of molecular mass from 2000 to 10,000 g/mol.

According to another advantageous embodiment of the composition used in stoppers in accordance with the invention, the structuring agent is chosen from the group comprising resinous compounds with a polymeric 15 and/or cyclic structure and which can contain, in minor proportion, aromatic derivatives and cyclic terpenes.

According to another advantageous embodiment of the composition in accordance with the invention, the structuring agent is chosen from the group of those 20 identified in Table A below, some of which are waxes or oils of natural or synthetic origin.

TABLE A

Origin of the structuring agent	Majority chemical nature of the structuring agent	Name of the structuring agent	Melting point (°C)	Density at 25°C ASTM D 1298	Penetration index at 25°C ASTM D 1321
Natural	ester (myricyl cirotate)	Carnauba	83-86	0.995	-
	ester (myricyl palmitate)	beeswax	62-65	0.955	-
Mineral	paraffinic hydrocarbons (mixture)	paraffin	50-60	0.900	15

	isoparaffinic and naphthenic hydrocarbons	micro-crystalline wax	69	0.930	29
	aliphatic hydrocarbons (mixture)	petrolatum	70-72	0.910/20°C	43-45
Synthetic	polyethylene	polyethylene wax	88	0.930	6.5
	oxidized isoparaffinic hydrocarbons	oxidized micro-crystalline wax	85	-	13
	phosphoric ester of C ₁₆ /C ₁₈ fatty alcohols	-	83-89	0.998	-
	polyethylene glycol	polyethylene glycol 4000	57-59	1.112/99°C	-

According to another advantageous embodiment, the composition used in the stoppers in accordance with the invention comprises at least one volatile corrosion inhibitor chosen from the group comprising:

- nitrogenous derivatives and in particular, firstly, aliphatic, aromatic, acyclic or cyclic amines including dicyclohexylamine, cyclohexylamine, morpholine, diisopropylamine and benzylamine, their organic salts including the benzoates, carbamates, laurates, caprylates and succinates, or their inorganic salts including the nitrites, nitrates, carbonates, phosphates and phosphites, and, secondly, heterocycles including imidazole and its derivatives, triazoles and their derivatives, as well as hexamethylenetetramine,
- nitrogenous oxido derivatives including the alkali metal or alkaline-earth metal salts of nitrous acid, and
- benzoic derivatives of these metals, such as sodium benzoate.

It is possible to include in the composition used in the stoppers in accordance with the invention

and/or in the stoppers one or more adjuvants chosen from the group comprising:

- antioxidants and/or degradation inhibitors including bisphenol A, butyl-hydroxytoluene, di-tert-butyl phosphite, trinonyl phenoxyphosphite and dilauryl thiodipropionate,
- anti-UV absorbing agents including benzotriazoles, triazines, hydroxybenzophenones and radical inhibitors including SHAs or Sterically Hindered Amines and HALS "Hindered Amine Light Stabilizers",
- external antistatic agents including phosphoric ethers of ethoxylated alcohols and ethoxylated amine chlorides, or internal antistatic agents including ethoxylated fatty amines, ethoxylated polyols and alkyl sulphonates,
- external or internal lubricants including paraffins, fatty alcohols, fatty acids, esters of fatty alcohols and acids, and amides,
- plasticizers including dioctyl phthalate, tricresyl phosphate and diesters of aliphatic acids,
- inorganic pigments including $PbSO_4$, $PbCrO_4$, $CdS.ZnS$, organic pigments including azo derivatives, phthalocyanins or anthraquinones, and
- flame retardants including bromo and chloro phosphorus compounds, hydrides of Al, Mg and Zn compounds, as well as epoxy oligomers,
- mineral fillers including chalks and carbonates, talcs, clays and silicas.

These adjuvants can also be added solely at the time of the incorporation of the composition into the polymer from which the stoppers in accordance with the invention are manufactured, or into the structuring agent from which the stoppers in accordance with the invention are manufactured.

These stoppers are characterized in that at least one of their components consists of a composition described above and in that they are prepared from at

least one polymer which constitutes at least 50% of their weight.

The abovementioned polymers which constitute at least 50% of the mass of the stoppers in accordance 5 with the invention can be chosen from those of the group comprising:

- polyolefins including polyethylenes, polypropylene, polybutene and their copolymers with one or more unsaturated monomers including vinyl acetate, 10 acrylic acid and its esters with carbon-based short-chain alcohols,
- polyvinyl chloride and its copolymers, acrylic copolymers and their derivatives, and
- polyamides, polystyrenes, polycarbonates, 15 polyesters, polyurethanes, rubbers including natural rubber, styrene-butadiene and polychloroprene.

The process for preparing these stoppers generally comprises, successively, a step of preparation of a composition or preblend based on 20 volatile corrosion inhibitors in accordance with the invention and a subsequent step during which the preblend is incorporated into one of the abovementioned polymers, the stoppers being obtained in particular by extrusion, moulding, injection-moulding or 25 thermoforming from the blend comprising the preblend and the polymer.

The stoppers are used for protecting the internal parts of hollow metal components that are sensitive to corrosion, during their transportation or 30 storage, without an additional protective treatment being applied to these components.

The invention may be understood more clearly with the aid of the non-limiting examples which follow, and which concern advantageous embodiments.

35

EXAMPLE 1

For the preparation of a VCI, 70 g of sodium nitrite, 17.5 g of benzotriazole and 12.5 g of ammonium benzoate are mixed together and then micronized in an

air-jet micronizer to give 100 g of homogeneous powdery mixture referred to as [1a] and having an average particle size of between 1 and 15 μm ; this powder constitutes a VCI.

5 In a heating tank fitted with a rotating stirrer and scraper, 226 g of the paraffin defined in Table A are melted at 65°C, after which 100 g of powder [1a] are incorporated into the molten mass and carefully dispersed.

10 2 g of anti-UV agent (sold under the brand name Tinuvin 622 LD by Ciba Geigy), 2 g of antioxidant - degradation inhibitor (sold under the brand name Chimassorb 944 LD by Ciba Geigy) and 3 g of yellow dye Colour Index PY10401/70, are then added.

15 The dispersion is prepared with stirring at a speed of between 300 and 500 rpm, for 10 minutes.

20 The 333 g of the mixture thus obtained, which constitutes a preblend [1b], are poured for cooling onto a laboratory flaking machine maintained at 10°C, and are then cut into flakes of between 0.5 and 10 mm in size.

25 300 g of preblend [1b] are homogeneously cold-blended with 5.7 kg of low-density polyethylene ($d=0.925 \text{ g/cm}^3$ and melt index $MI=20 \text{ g/10 minutes}$); the mixture obtained is injected at a temperature ranging between 145 and 160°C into a mould whose nest is cooled to 40°C, mounted on a Krauss Maffei series C - 40 t injection-moulding machine, with hydraulic closure (400 kN) and which works at a rate of 30 beats/minute; 30 the residence time of the molten material in each of the six zones of the cylinder is 15.6 seconds.

35 The finished article obtained is yellow VCI capsules, referred to as [1c], with a diameter of 20 mm, a thickness of 1 to 3 mm and a mass of 1 g, which are used for protecting the cavities and threaded parts of motor vehicle engines.

The volatile anti-corrosion efficacy of these VCI capsules [1c] was tested on mild steel test pieces, in the form of pins; the test used involves two

capsules and corresponds to US standard FED-STD 101, method 4031B.

This test method consists in placing a steel pin in a confined atmosphere charged with VCI released 5 from the film, and then in bringing about, by controlled cooling, condensation at the surface of the pin in order to bring about a possible oxidation after a determined time. The degree of rusting indicates the anti-corrosion efficacy of the stopper with regard to 10 the material constituting the pin.

After this test, it is found that the steel pin protected with the corrosion-inhibiting vapours which are released from the two VCI capsules [1c] shows no oxidation on its surface.

15 The same test was carried out, for comparative purposes, using "control" capsules, referred to as [1d], which are identical in all respects to the capsules [1c], except for the fact that they contain no VCI [1b] identified above; the 100 g of powder [1a] 20 forming part of the composition of the preblend [1b] were replaced with 100 g of mineral filler based on calcium carbonate.

After the test, the pin protected with the control capsules [1d] is completely attacked: many 25 blisters and rust are found over 100% of its surface.

EXAMPLE 2

For the preparation of a VCI, 300 g of preblend [1b] defined in Example 1 are homogeneously cold- 30 blended with 5.7 kg of low-density polyethylene ($d=0.925 \text{ g/cm}^3$ and melt index $MI=20 \text{ g/10 minutes}$); the blend obtained is injected at a temperature ranging from 135 to 150°C into a mould whose nest is cooled to 40°C, melted on a Krauss Maffei series C - 40 t 35 injection-moulding machine, with hydraulic closure (400 kN), working at a rate of 60 beats/minutes; the residence time of the molten material in each of the six zones of the cylinder is 9.9 seconds.

The finished article obtained is yellow VCI stoppers, referred to as [2c], with a diameter of 55 mm, a thickness of 1.5 mm and a mass of 6.5 g, which are used for protecting the cavities and threaded parts 5 of motor vehicle engines.

The volatile anti-corrosion efficacy of these VCI stoppers [2c] was tested on mild steel test pieces, in the form of pins; the test used involves one third of the stopper, i.e. 2.2 g, and corresponds to US 10 standard FED-STD 101, method 4031B, described in Example 1.

After this test, it is found that the steel pin protected with the corrosion-inhibiting vapours which are released from the VCI stopper [2c] shows no 15 oxidation on its surface.

The same test was carried out, for comparative purposes, using a "control" stopper, referred to as [2d], which is identical in all respects to the stopper [2c], except for the fact that it contains no VCI [1b] 20 identified above; the 100 g of powder [1a] which form part of the composition of the preblend [1b] were replaced with 100 g of mineral filler based on calcium carbonate.

After the test, the pin protected with control 25 stopper [2d] is completely attacked: many blisters and rust are found over 100% of its surface.

CLAIMS

1. Polymer-based stopper, characterized in that it incorporates a composition or preblend based on volatile corrosion inhibitors which comprises an effective amount of at least one structuring agent consisting of a solid or pasty substance whose melting point is from 40 to 110°C, preferably from 50 to 90°C.
5
2. Stopper according to Claim 1, characterized in that it incorporates a composition or preblend, comprising from 1 to 90%, preferably from 20 to 60%, by weight of at least one volatile corrosion inhibitor and from 10 to 99%, preferably from 40 to 80%, of at least one structuring agent consisting of a solid or pasty substance whose melting point is from 40 to 110°C, preferably from 50 to 90°C.
10
3. Stopper according to either of Claims 1 and 2, characterized in that it incorporates a composition or preblend whose solid or pasty structuring agent is chosen from the group comprising solid or pasty, aliphatic and/or resinous compounds with a low melting point of between 40 and 110°C, preferably between 50 and 90°C.
15
4. Stopper according to one of Claims 1 to 3, characterized in that it incorporates a composition or preblend whose solid or pasty structuring agent is chosen from the group comprising mono- or polyfunctional aliphatic compounds which are linear and/or slightly branched with hydrocarbon-based chains containing at least 10 carbon atoms.
20
5. Stopper according to Claim 4, characterized in that it incorporates a composition or preblend whose structuring agent is chosen from the group comprising:
 - saturated or unsaturated, optionally oxidized mono- or dicarboxylic acids, their esters and their salts,
35
 - phosphoric, sulphonic and phosphonic acids, their esters with alcohols and their alkali metal,

alkaline-earth metal, zinc, aluminium and/or organic amine salts,

- cyclic or acyclic compounds of the group comprising lactones, ketones, aldehydes, amides and 5 acetals,

- optionally polyalkoxylated, cyclic or acyclic, primary or secondary higher alcohols with a hydrocarbon-based chain containing at least 10 carbon atoms,

10 - linear and/or slightly branched aliphatic hydrocarbons, in particular paraffins and isoparaffins,

- polyolefins and their copolymers with low molecular masses from 3000 to 20,000 g/mol,

- polyglycols, in particular polyethylene 15 glycols of molecular mass from 2000 to 10,000 g/mol.

6. Stopper according to Claim 4, characterized in that it incorporates a composition or preblend whose structuring agent is chosen from the group comprising resinous compounds with a polymeric and/or cyclic 20 structure and which can contain, in minor proportion, aromatic derivatives and cyclic terpenes.

7. Stopper according to one of Claims 1 to 6, characterized in that it incorporates a composition or preblend whose structuring agent is chosen from the 25 group of those identified in Table A below, some of which are waxes of natural or synthetic origin:

TABLE A

Origin of the structuring agent	Majority chemical nature of the structuring agent	Name of the structuring agent	Melting point (°C)	Density at 25°C ASTM D 1298	Penetration index at 25°C ASTM D 1321
Natural	ester (myricyl cirotate)	Carnauba	83-86	0.995	-
	ester (myricyl palmitate)	beeswax	62-65	0.955	-

Mineral	paraffinic hydrocarbons (mixture)	paraffin	50-60	0.900	15
	isoparaffinic and naphthenic hydrocarbons	micro-crystalline wax	69	0.930	29
	aliphatic hydrocarbons (mixture)	petrolatum	70-72	0.910/20°C	43-45
Synthetic	polyethylene	polyethylene wax	88	0.930	6.5
	oxidized isoparaffinic hydrocarbons	oxidized micro-crystalline wax	85	-	13
	phosphoric ester of C ₁₆ /C ₁₈ fatty alcohols	-	83-89	0.998	-
	polyethylene glycol	polyethylene glycol 4000	57-59	1.112/99°C	-

8. Stopper according to one of Claims 1 to 7, characterized in that it incorporates a composition or preblend comprising at least one volatile corrosion inhibitor chosen from the group comprising:

5 - nitrogenous derivatives and in particular, firstly, aliphatic, aromatic, acyclic or cyclic amines including dicyclohexylamine, cyclohexylamine, morpholine, diisopropylamine and benzylamine, their organic salts including the benzoates, carbamates, laurates, caprylates and succinates, or their inorganic salts including the nitrites, nitrates, carbonates, phosphates and phosphites, and, secondly, heterocycles including imidazole and its derivatives, triazoles and their derivatives, as well as hexamethylenetetramine,

10 - nitrogenous oxydo derivatives including the alkali metal or alkaline-earth metal salts of nitrous acid, and

- benzoic derivatives of these metals, such as sodium benzoate.

9. Stopper according to one of Claims 1 to 8, characterized in that it consists of at least one 5 polymer which constitutes at least 50% of its weight and which can be chosen from those of the group comprising:

- polyolefins including polyethylenes, polypropylene, polybutene and their copolymers with one 10 or more unsaturated monomers including vinyl acetate, acrylic acid and its esters with carbon-based short-chain alcohols,

- polyvinyl chloride and its copolymers, acrylic copolymers and their derivatives, and

15 - polyamides, polystyrenes, polycarbonates, polyesters, polyurethanes, rubbers including natural rubber, styrene-butadiene and polychloroprene.

10. Stopper according to one of Claims 1 to 9, characterized in that it is incorporated by any 20 suitable process including moulding, injection-moulding, extrusion or thermoforming.

11. Use of the stoppers according to one of Claims 1 to 10 for protecting the internal parts of hollow metal components against corrosion.

STOPPER INCORPORATING A COMPOSITION OR PREBLEND BASED
ON VOLATILE CORROSION INHIBITORS

5 **ABSTRACT**

The invention relates to a polymer-based stopper, characterized in that it incorporates a composition or preblend based on volatile corrosion inhibitors which comprises an effective amount of at least one structuring agent consisting of a solid or pasty substance whose melting point is from 40 to 110°C, preferably from 50 to 90°C.

The invention is also directed towards the use of the said stopper for the internal protection of hollow metal components against corrosion.

20 No figures.

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

Docket No. 2-1032-184

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled, STOPPER INCORPORATING A COMPOSITION OR PREBLEND BASED ON VOLATILE CORROSION INHIBITORS, the specification of which(check) is attached hereto. was filed on _____ as Application Serial No. _____
and was amended on _____ (if applicable). was filed as PCT international application Number _____ on _____
and was amended under PCT Article 19 on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information known to me to be material to patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application (s) designating at least one country other than the United States of America listed below and have also identified below any foreign application for patent or inventor's certificate or of any PCT international application (s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application on which priority is now claimed:

Prior Foreign Application(s)		Priority Claimed
99 10087	FRANCE	<input checked="" type="checkbox"/> 03/08/1999
(Number)	(Country)	(Day/Month/Year Filed)
_____	_____	_____
(Number)	(Country)	(Day/Month/Year Filed)
_____	_____	_____
(Number)	(Country)	(Day/Month/Year Filed)
_____	_____	_____

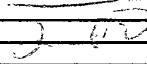
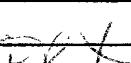
I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

PCTFRO0/02197	31-07-2000	(Status--patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status--patented, pending, abandoned)
_____	_____	_____
(Application Serial No.)	(Filing Date)	(Status--patented, pending, abandoned)
_____	_____	_____

I hereby appoint the following attorney(s) and/or agents(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: H. Robert Henderson, Reg. No. 18,486; Michael O. Sturm, Reg. No. 26,078; John E. Cepican, Reg. No. 26,851; Richard L. Fix, Reg. No. 28,297; William H. Wright, Reg. No. 26,424; Martin G. Mullen, Reg. No. 28,574; Daniel B. Greenwood, Reg. No. 35,885; and Curtis A. Bell, Reg. No. 36,742.

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Washington, DC 20004-1707

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor, Gabriela STOIANOVICIInventor's signature Date 10.01.2002Residence 95210 SAINT-GRATIENCitizenship FRENCHPost Office Address 2 rue du Général Leclerc, 95210 SAINT-GRATIEN (France)Full name of second joint inventor, if any Loïc GUILLOUSecond Inventor's signature Date 10.01.2002Residence 78400 CHATOUCitizenship FRENCHPost Office Address 25 A, rue Derain, 78400 CHATOU (France)Full name of third joint inventor, if any Patrick DRONIQUThird Inventor's signature Date Residence 92700 COLOMBESCitizenship FRENCHPost Office Address 5 ter rue Tilly, 92700 COLOMBES (France)

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

Docket No. 2-1032-184

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and was amended on _____ (if applicable). was filed as PCT international application Number _____ on _____
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I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information known to me to be material to patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

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Prior Foreign Application(s)			Priority Claimed
99 10087	FRANCE	03/08/1999	<input checked="" type="checkbox"/> Yes No
(Number)	(Country)	(Day/Month/Year Filed)	
_____	_____	_____	Yes No
(Number)	(Country)	(Day/Month/Year Filed)	
_____	_____	_____	Yes No
(Number)	(Country)	(Day/Month/Year Filed)	
_____	_____	_____	Yes No

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PCT_FR00/02197	31-07-2000	(Status--patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status--patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status--patented, pending, abandoned)

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Full name of sole or first inventor: Gabriela STOIANOVICI

Inventor's signature _____

Date _____

Residence 95210 SAINT-GRATIENCitizenship FRENCHPost Office Address 2 rue du Général Leclerc, 95210 SAINT-GRATIEN (France)Full name of second joint inventor, if any Loïc GUILLOU

Second Inventor's signature _____

Date _____

Residence 78400 CHATOUCitizenship FRENCHPost Office Address 25 A, rue Derain, 78400 CHATOU (France)Full name of third joint inventor, if any Patrick DRONIQUThird Inventor's signature 3-12Date 10 January 2002Residence 92700 COLOMBESCitizenship FRENCHPost Office Address 5 ter rue Tilly, 92700 COLOMBES (France)